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On the volume change on non covalent gels in solvent–non solvent mixtures

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SUMMARY

In this paper, the volume change on polysaccharide gels in non solvent mixtures is investigated. No phase transition is observed. A reversible decrease of the swelling volume is obtained directly related to the mechanical properties of the gels and to the charge parameters of the polymers. The effect of deswelling in presence of acetone or alcohol is increasing from agarose, k-carrageenan and i-carrageenan.

INTRODUCTION

Tanaka and coworkers (1-5) investigated the volume changes on covalent neutral and ionic networks ; they described volume changes taking place when temperature (1), pH (2), salt concentration (3) and solvent composition are changed. The swelling ratio φ^*/φ of the volume fraction occupied by the network in the gel before (φ^*) and after (φ) the volume change were obtained by measuring the volume of the gel before (V*) and after (V) the volume change (with $\varphi^*/\varphi = V/V^*$).

The swelling ratio on polyacrylamide gels undergoes a discrete transition around 40 % when the acetone concentration of water-acetone mixtures increases (1). On the polyacrylamide partially hydrolyzed, it is shown that ionization plays an essential role in the phase transition (2); a discontinuous phase transition can be observed depending on proportion of ionizable groups and stiffness of the polymer chains constituting the network (3,5).

In this work, the volume changes of non covalent gels formed with polysaccharides in water are studied in organic solvent-water mixtures. The organic solvents used (acetone, methanol or ethanol) are non solvent of the polysaccharides.

EXPERIMENTAL

Purified agarose from Marine colloïds (U.S.A.), K and i-carrageenans from MRS (France) are used to form the gel in water and external salt when necessary to stabilize the gel ; the experimental conditions are given in Table 1.

The volume of the gel pieces after equilibrium in given organic solvent-water mixtures are determined from weight measurements (taking into account the density of the solvent) or from dimension measurements on photographs. Equilibrium time varies from 10 to 40 days for i-carrageenan and agarose respectively.

The pieces of gel are prepared with constant diameter (12 mm) and height (7 mm), before immersion in the different solvent mixtures studied.

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TABLE I : Experimental conditions

Polymer	Non solvent	Initial aqueous solution composition External salt	Polymer concentration
Agarose	Acetone	NO	5 g/l
	Methanol	NO	5 g/l
K-carrageenan	Acetone	0.1 M KCl	5 g/l
i-carrageenan	Ethanol	0.25M KNO_3	20 g/l

RESULTS AND DISCUSSION

Neutral agarose and ionic K-carrageenan are well known polysaccharides which form firm non covalent gels in well defined conditions (see Table 1). The network junctions are formed by aggregation of helical dimers (6) based on thermodynamic properties of the systems. With i-carrageenan, more soft gels are formed ; these gels are less stable than that of K-carrageenan due to their higher charge density. Solvents as acetone, ethanol or methanol are non solvent for these polysaccharides ; when added to aqueous solution of K and i-carrageenans even in absence of external salt, they induce the coil-helix conformational transition and then gelation. These solvents have no disruptive effect on the polymer secondary conformation. When pieces of polysaccharidic gels are equilibrated in these organic solvent-water mixtures, discrete volume changes are obtained without any phase transition. The variation of swelling expressed by V*/V are plotted for the different systems in Figure 1.

In the three cases, the volume change is fully reversible ; the skrinking of the gels varies much with the chemical structure of the gel. The volume decrease is very small (V*/V $\sim$ 1.2) with the stiff neutral agarose gel and is the same in acetone or methanol.

The effect of non solvent is more important when the charge density increases and when the stiffness decreases for K-carrageenan (one sulfate group per disaccharide unit) (V*/V $\sim$ 4) and i-carrageenan (two sulfate groups per disaccharide unit) (V*/V $\sim$ 19).

The deswelling begins for non solvent content depending on the charge density : 20% H_2O on agarose, 70 % on K-carrageenan, traces of non solvent on i-carrageenan.

CONCLUSION

No phase transition was observed on the polysaccharidic non covalent gels in opposition with the synthetic covalent gels investigated by Tanaka et al. As soon as the helical stiff conformation is stable, the rigid networks present only small volume changes in solvent - non solvent mixtures, specially for the neutral polysaccharides. In addition, the role of strong water molecules interactions in these polysaccharides is surely important on the behaviour observed (7).

The volume and morphology changes on the gels are reversible in the experimental conditions investigated which are selected such as to preserve the physical junction zones.

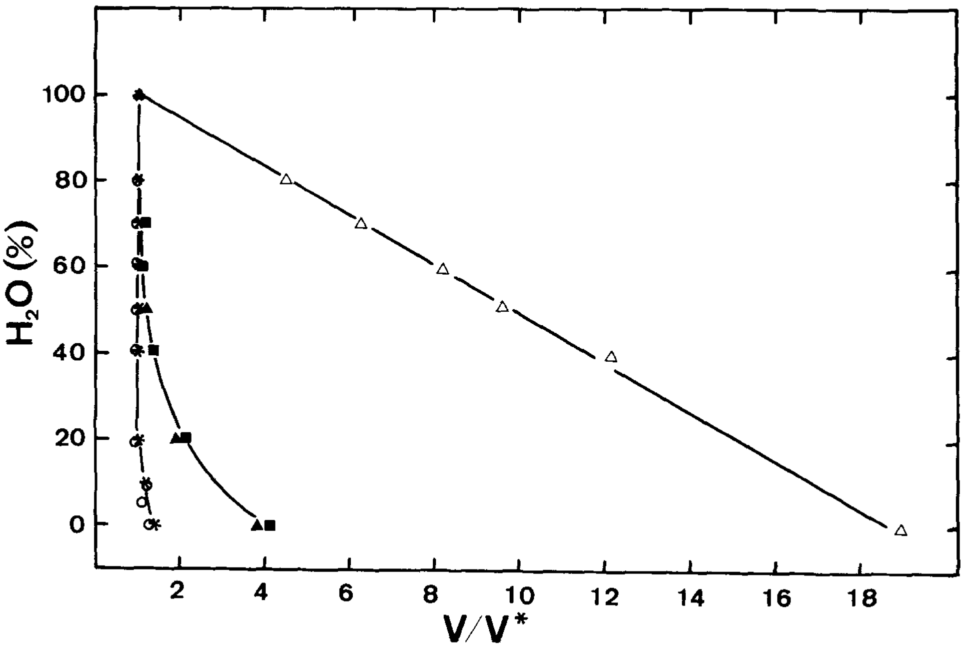

Figure 1 : Dependence of the ratio (V/V*) with the solvent composition after equilibrium
a) from weight determination ○ Agarose ■ K-carrageenan
△ i-carrageenan
b) from photographs * Agarose ▲ k-carrageenan

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